



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

REGION 5

AIR AND RADIATION DIVISION

77 WEST JACKSON BOULEVARD

CHICAGO, IL 60604-3590

**DATE:** April 20, 2001

**SUBJECT:** Inspection  
Report for S.H. Bell Co. in East Liverpool, Ohio

**FROM:** Margaret Sieffert, Environmental Engineer  
Air Enforcement and Compliance Assurance Section (MN/OH)

**THRU:** William MacDowell, Chief  
Air Enforcement and Compliance Assurance Section (MN/OH)

**TO:** File

Date of Inspection:  
February 22, 2001

Source Name and Locations:  
S.H. Bell Company (Stateline)  
2217 Michigan Avenue  
East Liverpool, OH, 43920  
  
S.H. Bell Company (Little England)  
1 Saint George Street  
East Liverpool, OH, 43920

Participants:  
Rusty Davis, Terminal Manager, S.H. Bell Company  
John Bedeck, Project Engineer, S.H. Bell Company  
Darren Machuga, District Representative, OEPA-NEDO  
Margaret Sieffert, Environmental Engineer, U.S. EPA  
John Shepler, Environmental Engineer, U.S. EPA

I. Purpose and Scope of Inspection

On February 22, 2001, staff from the United States Environmental Protection Agency (U.S. EPA) along with a representative from the Ohio Environmental Protection Agency (OEPA) Northeast

District Office (NEDO) performed an unannounced inspection of the S.H. Bell Company (S.H. Bell) facility located in East Liverpool, Ohio. The primary objective of the inspection was to obtain visual knowledge of the facility after receiving a recent Section 114 response and assist in determining S.H. Bell's compliance status with respect to the Clean Air Act (CAA), the Ohio State Implementation Plan (OH SIP), and permits issued by the OEPA incorporating the provisions of the CAA and the OH SIP. Mr. Rusty Davis of S.H. Bell, granted U.S. EPA and OEPA-NEDO entry into the facility and led the facility tour with Mr. John Bedeck.

## II. Arrival and Opening Conference

U.S. EPA arrived at S.H. Bell, at approximately 8:20 a.m., and checked in. Mr. Davis greeted us soon after our arrival and we began our opening conference.

After introductions, Mr. John Shepler and Ms. Margaret Sieffert, of U.S. EPA, presented our credentials, stated the purpose for the inspection and informed S.H. Bell that if the company wished to claim confidentiality on anything presented during the inspection, the company needed to tell us and we would mark our notes.

Mr. Shepler stated that U.S. EPA recently issued S.H. Bell a second Section 114 Information Request and would like a tour of the facility to become familiar with the processes described in the first Section 114 Information Response.

## III. General Facility

S.H. Bell's corporate headquarters is located in Pittsburgh, Pennsylvania. They own and operate six facilities which are located in Braddock, Pennsylvania; East Liverpool, Ohio; Chicago, Illinois; Lake Calumet, Illinois; and Newell, West Virginia.

S.H. Bell began operations at its two East Liverpool facilities in 1963. S.H. Bell markets handling and temporary storage space of ferrous and nonferrous materials for industry. These materials are transferred to and from the site via railcars, trucks, and barges. The East Liverpool facilities also provide other basic material handling services such as particle size reduction, screening, and drying. There are 76 employees and they work two shifts. The Stateline facility has 90 acres and the Little England facility has 10 acres. They have 150 customers.

## IV. Process Description

Process descriptions are taken from S.H. Bell's 114 Information Response and notes taken during inspection.

Stateline Facility - Ohio Side

*West and East Bag Filling Stations* - These operations are used to fill small (<50 lb) packages. Material is dumped into a hopper by a front end loader. A vibratory feeder is used to feed the material through a small chute, and into the package. The package is then closed.



*Trico Filling Unit* - This system is also used to fill various packages. Material is dumped into a hopper by a front end loader. A covered belt conveyor transports the material to a chute, and into the package.

There is a total of 4 packaging and filling stations. Two are for small bags and two are for supersaks and drums. The systems are controlled by baghouses which are vented outside the building.

*Area C Crushing* - This operation consists primarily of a jaw crusher and a double deck screener. Material is removed from a storage location and dumped into the dump hopper by a front-end loader. The crusher is fed by a vibratory feeder. Dust suppression foam is used to control dust at the crusher and selected transfer points. The crushed material is discharged onto a covered conveyor and transported to the crusher screener enclosure. The material is then run across the screener and discharged into bins. The screener and bins are inside the enclosure. Once screened, the material is either returned to storage, re-crushed or shipped. According to Mr. Davis, last year this unit was operated 60-100 hours/week.

*Area C Screener* - This operation consists primarily of a grizzly feeder and a double deck screener. Material is removed from storage and dumped into the hopper by a front-end loader. Material is then fed across the grizzly feeder. Material that falls through the fingers is directed onto a covered conveyor and transported to the screener enclosure. This material is then discharged onto the screener, and separated into three storage bins (inside the enclosure). The material that did not fall through the grizzly is either transported to a separate storage pile, or conveyed into one of the screened piles inside the screener enclosure. The material is then returned to storage or shipped. According to Mr. Davis, last year this unit was operated 60-100 hours/week.

*PA Crusher* - This operation consists of a jaw crusher and a conveyor. Material is fed into the crusher via a vibratory feeder. The crushed material is discharged onto a conveyor belt and transported to a covered storage pile. This material is then re-crushed, returned to storage, or shipped. According to Mr. Davis, this unit has not been operated for approximately 6 months.

*PA Screener* - This operation consists of a double deck screener and conveyor belts. Material is fed onto the screener by a vibratory feeder, and separated into three sizes. Each size is discharged onto conveyors and transported to storage bins. This system is surrounded by an enclosure. According to Mr. Davis, last year this unit was operated for approximately 16 hours/week.

*Rotary Dryer* - Material is fed onto a belt conveyor from the dump hopper via a vibratory feeder. As the material to be dried enters the rotating drum, it is advanced through the drum by means of a suction fan and continues bouncing on the drum's inside surface. The material is moved forward by the movement of the heated air. Moisture is removed from the material during this process. When leaving the rotary drum, the material is transported in the air stream to a settling chamber where separation of the air and material is accomplished. This material is discharged onto the exit conveyor. The air then goes through a cyclone for additional fines separation. The cyclone also discharges on the exit conveyor. Finally, the air stream is pulled through two baghouses. The two baghouses have one venting inside the building and one venting outside. The material that is discharged onto the exit conveyor is transported into the screener enclosure and run across a single deck screen. This system is inside a building. The Rotary Dryer was operating during the inspection.

*Carmen Palletizing Station* - This system is used to fill various packages. Material is dumped into a hopper by a front-end loader. A vibratory feeder is then used to fill the packages.

*Raildock Conveyor* - The raildock conveyor consists primarily of a covered belt conveyor. Material is dumped into a hopper by a front-end loader, and is directly discharged onto the covered conveyor. From the conveyor, the material is discharged through an adjustable loading spout, and into either pneumatic trucks or railcars.

*Raildock Unloading* - Bulk material is unloaded from railcars into hopper-pits. This process is done inside an enclosure.

*Raildock Loading* - Bulk material is loaded into railcars either by a front-end loader or the Raildock Conveyor listed above. The control device used on this unit a baghouse.



The Railyard area handles 10-15 railcars/month.

*Screen-Box* - A screen box is a steel frame with an inclined screen. Material is slowly dumped onto the screen by a front-end loader, where the fines pass through, and the top size rolls off. This process is used to roughly scalp material. This material is either sent to a separate process, shipped, or returned to storage.

*River Barge Crane Unloading* - Bulk material is unloaded from a barge one of two ways. Depending on the material, a clam bucket is used, or a dump pan. The dump pan required a front-end loader inside the barge to fill the pan and the crane transfers the material to the dock area and dumps it. The clam bucket does not require the front-end loader. Once on the dock, the material is either moved to storage or shipped.

*Straight Sides Dock* - Material is unloaded from the barge with a hydraulic excavator and transferred directly to trucks for transport to storage or for shipping.

*Truck Loading Station* - There are four Ohio side truck unloading stations. At the SMC building, during the inspection, extensive fugitive emissions were present during the loading of a truck with magna-site.

*Storage Piles* - There are approximately 600-700 inside bins and 100 outside bins. About half are in Ohio and the others are in Pennsylvania. Products can sit for 2-3 days, 3 months, or over a year.

#### *Stateline Facility - Pennsylvania Side*

*KUX Crusher* - Material is dumped into the hopper via a front-end loader, and fed into the crusher by a vibratory feeder. Once crushed, the material falls into a storage bin. The crushed material is either re crushed, screened at a different operation, shipped or returned to storage. The control device used on the unit is foam suppression.

*Fine Size Screener* - Material is dumped into the hopper via a front-end loader, and fed into the enclosed screener by a vibratory feeder. The material is screened to four sizes, and is directed to the appropriate storage hopper via chutes. The material is then fed into trucks or front-end loaders by

vibratory feeders and returned to storage or shipped. The control device used on the unit is a baghouse.

*Screen Box* - A screen box is a steel frame with an inclined screen. Material is slowly dumped onto the screen by a front-end loader, where the fines pass through, and the top size rolls off. This process is used to roughly scalp material. This material is either sent to a separate process, shipped, or returned to storage.

*River Barge Crane Unloading* - Bulk material is unloaded from a barge one of two ways. Depending on the material, a clam bucket is used, or a dump pan. The dump pan requires a front-end loader inside the barge to fill the pan and the crane transfers the material to the dock area and dumps it. The clam bucket does not require the front-end loader. Once on the dock, the material is either moved to storage or shipped. During the inspection one barge was unloading coils and another one was loading supersacs.

*Truck Loading Station* - There are three Pennsylvania side truck unloading stations. One unloading station is controlled by a fabric collector. The Pennsylvania Department of Environmental Protection required S.H. Bell to install the fabric collector.

#### *Little England Facility*

*Kue-Ken Crushing and Screening System* - This operation consists primarily of a jaw crusher and a double deck screener. Material is removed from a storage location and dumped into the dump hopper by a front-end loader. The crusher is fed by a vibratory feeder. Dust suppression foam is used to control dust at the crusher and selected transfer points. The crushed material is discharged onto a covered conveyor and transported to the crusher-screener enclosure. The material is then run across the screener, and discharged into bins. The screener and bins are inside the enclosure. Once screened, the material is either returned to storage, re-crushed or shipped. The Kue-Ken Crushing and Screening unit processes all products. According to Mr. Davis, last year this unit operated an average of 40 hours/week. It sometimes was operated 60-80 hours/week.

*Simplicity Screener* - Material is dumped into the hopper via a front-end loader, and is fed onto a covered conveyor belt by a grizzly feeder. The material is then transported to a double deck screener where it is separated into three sizes. Each



sized material is then transferred into a separate storage bin by chutes. This screener material is then fed into trucks via vibratory feeders and transported to storage. Material that does not fall through the grizzly is discharged into a storage bin. The simplicity screener processes mostly ferro alloys. The control mechanism for this unit is foam suppression and building enclosure. According to Mr. Davis, last year this unit operated 8-16 hours/week.

*River Barge Crane Unloading* - Bulk material is unloaded from a barge one of two ways. Depending on the material, a clam bucket is used, or a dump pan. The dump pan required a front-end loader inside the barge to fill the pan and the crane transfers the material to the dock area and dumps it. The clam bucket does not require the front-end loader. Once on the dock, the material is either moved to storage or shipped.

*Hammermill* - Material is dumped into a hopper by a front-end loader. The material is transported to a single deck screen via a conveyor. Material that falls through the screen is dumped into a storage pile. Top size material is directed into a hammermill for size reduction either  $\frac{1}{2}$ " or  $\frac{1}{4}$ ". Once through the hammermill, the material is returned to the screener. The hammermill will not crush ferro chrome or ferro manganese. According to Mr. Davis, last year this unit operated 8-16 hours/week. The hammermill is controlled by a baghouse but the baghouse presently on it is undersized and a new baghouse was supposed to be installed by March 1, 2000.

*Storage Piles* - There are approximately 100 inside bins and 70-80 outside bins. Products can sit for 2-3 days, 3 months, or over a year.

*Boxing and Bagging System* - Material is dumped into the system and it is either boxed or bagged for shipment. This unit has a baghouse which is vented inside the building.

## V. Facility Tour

Mr. Davis and Mr. Bedeck led the tour. The processes were viewed first at the Little England facility and then the Stateline facility. Please see the descriptions above for other information related to each unit gathered during the facility tour.



S.H. Bell's roadways are watered by a contractor. C.A. Joseph Co. is the contractor. They use water from the river. According to Mr. Davis, the contractor is there from 7 am until 7 pm.

Mr. Davis said there are problems with foam suppression and they are trying water foggers.

#### VI. Records Review

No records were reviewed at the facility since they were being asked for in the Section 114 Information Request.

#### VII. Conclusion

During the post-tour interview, U.S. EPA told S.H. Bell that an inspection report will be written and if they wanted a copy they needed to request it through the Freedom of Information Act. Nothing further was discussed.

Standard bcc's: official file copy w/attachment(s)

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**To: Theresa Hosick, EPA/NEIC**

**Subject: Analytical Report on Analysis of Air Filter Samples for Hexavalent Chromium**

**Case No: EPA VP0591 – second sampling**

**From: Ruth E. Wolf, USGS**

**Date: January 22, 2009**

**Background:** Glass fiber air filters testing high in total Cr values were selected to be analyzed for  $\text{Cr}^{+6}$  via HPLC ICP-MS using a method recently developed at USGS (Wolf et.al.). Due to concerns that any  $\text{Cr}^{+6}$  present in the air filter samples might have been reduced to  $\text{Cr}^{+3}$  in the original set of samples (see June 24, 2008 report), the site was re-sampled using quartz filters pretreated with a 1N NaOH solution (done by T. Hosick at EPA NEIC) prior to sample collection to stabilize any  $\text{Cr}^{+6}$  if present. The samples were then extracted using the method described in the June 24, 2008 report and analyzed for  $\text{Cr}^{+3}$  and  $\text{Cr}^{+6}$ .

**Method of Analysis:** A detailed description of the method development work was given in the June 24, 2008 report to T. Hosick. A method developed at USGS for the determination of  $\text{Cr}^{+6}$  in natural waters, de-ionized water leachates of soil samples, and simulated gastric and lung fluid extracts of geological materials (Wolf, et. al., 2007) has been adapted for use in the determination of  $\text{Cr}^{+6}$  air filter samples. In summary, the method uses reversed-phase ion-pairing chromatography on a 3cm C8 column to separate the following species:  $\text{Cr}^{+3}$ ,  $\text{Cr}^{+6}$ ,  $\text{As}^{+3}$ ,  $\text{As}^{+5}$ ,  $\text{Se}^{+4}$ , and  $\text{Se}^{+6}$ . The HPLC mobile phase employed is 2 mM tetrabutylammonium hydroxide (TBAOH) with 0.5mM  $\text{K}_2\text{EDTA}$ , adjusted to pH 7.4 – 7.6. 5% methanol is added to the mobile phase by the HPLC pump. The EDTA present in the mobile phase is for the purposes of converting the Cr(III), which is present in aqueous solutions in a cationic form to an anionic Cr(III)-EDTA complex. All samples are diluted a minimum of 1:1 in the mobile phase and allowed to sit at room temperature to allow the Cr(III)-EDTA complex to form prior to analysis.

The final method used to evaluate this batch of samples is as follows:

1. One-inch sub-samples were taken from each air filter (cut parallel to void areas left by filter holder) and accurately weighed to 0.1 mg.
2. The filter samples were folded and placed in 50mL conical bottom centrifuge tubes (BD Falcon)
3. Duplicate blank samples from each box or lot of prepared quartz filters were taken to estimate procedural blank values.
4. Additional samples of prepared quartz filters were taken and spiked with 50  $\mu\text{L}$  of a 10 mg/L solution of  $\text{Cr}^{+6}$  (from 1000 mg/L stock solution of  $\text{K}_2\text{Cr}_2\text{O}_7$ , Spex Certiprep, NJ) and allowed to dry prior to extraction.
5. Additional blanks from 45mm quartz filters (Whatman #1851-047 Grade QMA, Lot #H11368033B) prepared by USGS with 1N NaOH and blank filters spiked with 50  $\mu\text{L}$  of a 10 mg/L solution of  $\text{Cr}^{+6}$  were weighed and added to 50 mL tubes for use as quality control samples.
  - a. The filters were first prepared by treating them with 1N NaOH (prepared from Fisher ACS reagent grade NaOH pellets, lot 051758, and de-ionized water (Milli-Q, 18 M $\Omega$ ) to enhance stability of  $\text{Cr}^{+6}$ . The filters were placed on a magnetic



filter holder and using a vacuum filter dome, approximately 2mL of 1N NaOH was placed on the filter. The vacuum was turned on and the 1N NaOH solution pulled through the filter. The rinsed filters were removed from the filter holder with plastic forceps and placed on laboratory wipes, covered and allowed to dry overnight.

6. Three 45mm prepared quartz filters were doped with small (10-30 mg) portions of NIST 2701 (Hexavalent Chromium in Contaminated Soil) that had been further micronized in June 2008 for possible use as a reference material. The micronized material was stored at room temperature since June 2008.
7. Three individual samples of BCR 545 – Hexavalent Chromium in Welding Dust Certified Reference Material prepared by IRMM (Belgium) were also added to individual 50 mL tubes for use as quality control samples. Samples of BCR 545 were stored at 4 ° C after receipt until used.
8. A stock 0.1M Na<sub>2</sub>CO<sub>3</sub> – 0.9M NaHCO<sub>3</sub> stock solution was prepared by dissolving 7.5609 g NaHCO<sub>3</sub> and 1.0599g Na<sub>2</sub>CO<sub>3</sub> (both ACS reagent grade) in de-ionized water (Milli-Q, 18 MΩ) in a 100 mL volumetric flask. Measured pH = 9.2. Contents of volumetric flask were transferred to a clean 125 mL HDPE bottle for long-term storage.
9. 1 L bottles of pH 9 carbonate extraction fluid were prepared as needed by diluting 10mL of the 0.1M Na<sub>2</sub>CO<sub>3</sub> – 0.9M NaHCO<sub>3</sub> stock solution prepared above to 1L with de-ionized water. pH was checked and was 9.3.
10. 50 mL of pH 9 carbonate extraction fluid was added to each 50mL tube containing a filter sample. The samples were immediately placed in a sonicator at room temperature for 3 hours. At the end of sonication, the bath temperature was approximately 60 ° C.
11. After sonication was complete, the sample tubes were then removed to a rack and allowed to cool to room temperature prior to filtration.
12. The HPLC mobile phase was prepared by diluting stock solutions of tetrabutylammonium hydroxide (TBAOH, 0.4M, Baker, Lot C056046) and 0.5M K<sub>2</sub>EDTA to 2mM TBAOH and 0.5mM EDTA in de-ionized water (Millipore Element A10). The pH of the mobile phase was adjusted to fall within the 7.5 – 7.6 range using 10% nitric acid and ammonium hydroxide solutions.
13. Calibration standards for Cr<sup>+3</sup>, Cr<sup>+6</sup>, Se<sup>+4</sup>, Se<sup>+6</sup> As<sup>+3</sup>, and As<sup>+5</sup>, species were prepared by successive dilution of 1000 mg/L stock solutions (Spex Industries, lots 14-124Cr(III), 14-152Cr(VI), 14-122SE(VI), 14-31SE(VI), 14-131AS+3, and 14-09AS5, respectively) in the mobile phase to reach a working stock concentration of 10 mg/L of each species. A combined stock containing all 6 species at 100 µg/L in the HPLC mobile phase was prepared with careful mixing in between the addition of each stock solution to avoid rapid pH shifts that can cause species transformation. The multi-component stock solution was then diluted in the mobile phase to prepare 0.1, 0.2, 0.5, 1, 2, 5, and 10 µg/L calibration and check standard solutions. Calibration solutions were allowed to sit for 30 minutes prior to use to allow the Cr<sup>+3</sup>-EDTA complex to form.
14. Independent calibration verification standards were prepared using 100 mg/L stock solutions of Cr<sup>+3</sup>, Cr<sup>+6</sup>, Se<sup>+4</sup>, Se<sup>+6</sup> As<sup>+3</sup>, and As<sup>+5</sup> in the same manner used for the calibration standards. Stock solutions were obtained from VHG labs, lots 704-0233R, 803-0328, 709-0672R, 704-0249R, 708-0464, and 704-0232R, respectively.
15. Prior to analysis, a 10 mL aliquot of each supernatant from the extraction tubes was drawn into a 10 mL disposable syringe (BD Dickinson). A 0.45 µm syringe type filters



(Pall, 25mm, Acrodisc, PDVF) was attached to the syringe and the extract was filtered into a new 15 mL polypropylene centrifuge tube.

16. All filtered sample extracts were diluted 1:5 with the mobile phase (100  $\mu$ L sample + 400  $\mu$ L mobile phase) and allowed to sit at room temperature for approximately 30 minutes to allow the Cr(III)-EDTA complex to form. A second 100  $\mu$ L aliquot of each extract was also prepared and diluted with 150  $\mu$ L of mobile phase and 250  $\mu$ L of the 5  $\mu$ g/L mixed species calibration standard. The purpose of this second spiked aliquot was to act as an analytical spike at 2.5  $\mu$ g/L. The recoveries of the species in the analytical spike were used to assess the impact of the sample matrix, if any, on the separation and could be used to account for any signal drift or enhancement due to the sample matrix over time. This was thought to be necessary since the instrument chromatographic software did not allow the use of a mass-spectral internal standard for multi-component analysis.
  - a. In the method development work done in June 2008, it was found that diluting all filtered extract solutions 1:1 with the HPLC mobile phase solution worked well. However, the increase in pH of the extraction solution due to the NaOH present on the prepared quartz air filters required further dilution to 1:5 in order to maintain adequate chromatographic separation of the Cr species. Samples were initially run at a 1:1 dilution and the resulting chromatographic separation was deemed inadequate for quantitation. The sample extracts and standards were refrigerated over night at 4° C prior to re-dilution and re-analysis at the 1:5 dilution.
17. Due to the known high levels of Cr<sup>+6</sup> present, extracts of BCR 545 and NIST 2701 were pre-diluted prior to dilution in HPLC vials and analysis. Separate aliquots of each reference material extract were diluted 1:10 and 1:50 in order to bring Cr<sup>+6</sup> concentrations into working calibration levels. These intermediate diluted extracts were then diluted 1:5 as the rest of the samples, above to result in a total dilutions of 1:50 and 1:250, respectively.
18. The extract solutions were analyzed via HPLC-ICP-MS under the following conditions:
  - a. TBAOH/EDTA mobile phase 95% - 5% MeOH (mixed by HPLC pump)
  - b. Flow rate 1.5 mL/min
  - c. Column temperature 35 ° C
  - d. Autosampler tray temperature 10 ° C
  - e. Injection volume, 50  $\mu$ L using 200  $\mu$ L
  - f. DRC conditions: N<sub>2</sub> reaction gas at 1.0 mL/min, rpq=0.5

Sample concentrations were calculated as  $\mu$ g Cr<sup>+6</sup>/ g filter.

**Preliminary Calculations:** Using the total Cr values provided by Theresa Hosick from EPA NEIC, the maximum possible concentration of Cr<sup>+6</sup> that could possibly be present after sample extraction and analysis by the HPCL-ICP-MS speciation method was calculated and are presented in the table below. Using a 1" strip subsample extracted into 50mL of solution with a 1:5 analytical dilution would result in maximum concentration levels above 3  $\mu$ g/L, as presented to the instrument. A concentration easily determined by the described analytical method. Even if only 10% of the Cr present was in the form of Cr<sup>+6</sup>, the analytical method should be able to detect the presence of Cr<sup>+6</sup> at the lowest estimated level of 0.3  $\mu$ g/L.

Filter number	Filter Collection Date	Cr DRC 52 ug/filter	Max Cr(VI) possible if all Cr is Cr(VI) in extract in ug/L		
			<i>undiluted</i>	<i>5x dilution</i>	<i>Speciation DL</i>
1	08/08/08	20.511	45.6	9.1	0.2
2	08/13/08	73.165	162.6	32.5	0.2
3	08/19/08	43.550	96.8	19.4	0.2
4		<4			0.2
5	08/25/08	69.439	154.3	30.9	0.2
6	09/04/08	126.419	280.9	56.2	0.2
7	09/10/08	176.717	392.7	78.5	0.2
8	09/16/08	20.334	45.2	9.0	0.2
9		<4			0.2
10	09/22/08	247.225	549.4	109.9	0.2
11	09/28/08	25.291	56.2	11.2	0.2
12	10/02/08	7.507	16.7	3.3	0.2
13	10/08/08	45.043	100.1	20.0	0.2
14	10/16/08	32.253	71.7	14.3	0.2

**Results for Quality Control Samples:** Average recoveries for the three samples of BCR 545 Cr<sup>+6</sup> reference material used as a quality control standard were 39,800 (±1640) µg/g for the 1:250 dilution and 40,800 (±490) µg/g for the 1:50 dilution. These values represent 99.0% and 101.5% recovery of the certified value, respectively. The NIST 2701 samples were not used as Quality Control materials due to low (50-70% recoveries) – possibly due to inadequate storage conditions of the material after micronizing in June 2008.

Recoveries for all Cr<sup>+6</sup> analytical spikes performed on EPA filter samples were acceptable (within ± 10% of spiked value) for all samples except EPA Filter 4 (blank filter) which was recovered at 112%, EPA filter 9 (blank filter) recovered at 88.4%, EPA Filter 10 (duplicate) recovered at 118%, and EPA Filter 15 recovered at 114%. In all samples analytical spike recovery was within ± 20% which is generally considered acceptable in other EPA methodologies (such as Method 6020A).

Recoveries for pre-extraction spikes of blank filters ranged from 100 – 140% recovery, which is slightly high; however these values are greatly impacted by the blank filter values which had a rather large standard deviation. The blank filters (n=4) averaged 0.77 (±0.29) µg/L in the extract solution. In general, all the Cr<sup>+6</sup> spiked onto the blank filters was recovered and no apparent conversion of Cr<sup>+6</sup> to Cr<sup>+3</sup> was observed.



# Results for Test Filter Samples:

RAW Data and QC spike results in ug/L extraction fluid (not dilution corrected)				Data in ug/ 1" strip - with dilution correction	Data in ug/filter - not blank subtracted	Data in ug/filter - Blank subtracted
Lab ID	Sample ID	Prep Dilution	CrVI ug/L	CrVI ug/strip	CrVI ug/filter	CrVI ug/filter
<i>200 ppt</i>			<i>PQL - Quantitation Limit</i>	<i>0.2</i>	<i>0.1</i>	<i>0.9</i>
Average Blank (A and B, n=4)			0.77	0.1925	1.73	
std dev Blanks			0.2945052	0.0736	0.66	
S1 5X	EPA 1	5x	0.44	0.1100	0.99	ND
S2 5X	EPA 2	5x	0.12	0.0300	0.27	ND
S3 5X	EPA 3	5x	0.43	0.1075	0.97	ND
S4 5X	EPA 4 - Blank	5x	0.75	0.1875	1.69	ND
S5 5X	EPA 5	5x	0.56	0.1400	1.26	ND
S6 5X	EPA 6	5x	0.51	0.1275	1.15	ND
S7 5X	EPA 6 Duplicate	5x	0.63	0.1575	1.42	ND
S8 5X	EPA 7	5x	0.22	0.0550	0.50	ND
S9 5X	EPA 7 DUPLICATE	5x	0.17	0.0425	0.38	ND
S10 5X	EPA 8	5x	0.25	0.0625	0.56	ND
S11 5X	EPA 9 BLANK	5x	0.72	0.1800	1.62	ND
S12 5X	EPA 10	5x	0.5	0.1250	1.13	ND
S13 5X	EPA 10 DUPLICATE	5x	0.53	0.1325	1.19	ND
S14 5X	EPA 10 TRIPLICATE	5x	0.46	0.1150	1.04	ND
S15 5X	EPA 11	5x	0.39	0.0975	0.88	ND
S16 5X	EPA 12	5x	0.46	0.1150	1.04	ND
S17 5X	EPA 13	5x	0.34	0.0850	0.77	ND
S18 5X	EPA 15	5x	0.33	0.0825	0.74	ND

ND = not detected above BLANK levels

SRM BCR 545		Dilution	Cr(VI) mean	std dev	% Recovery
BCR 545 Average	(stored in Fridge)	250x	39791.8	1642.1	99.0%
		50x	40813.2	489.8	101.5%
	True Value		40200	600	

NOTE: Cr+3 values are zero in the filtered extract solutions are zero as expected as the Cr+3 present would be present as Cr(OH)3 and would adsorb onto any solid particles and be filtered out. Cr+3 was recovered in all analytical spikes which where spiked with both Cr+3 and Cr+6.

In summary, looking at the column for “Data in  $\mu\text{g/g}$  filter – not blank subtracted” no filter samples contained any  $\text{Cr}^{+6}$  in excess of the average blank value of  $1.73 \mu\text{g Cr}^{+6}$ . It should be noted that any  $\text{Cr}^{+3}$  present would necessary be removed in the post extraction filtration step as it tends to form  $\text{Cr}(\text{OH})_3$  complexes which adhere to Fe and other metallic oxides that would be filtered out.

**References:**

Wolf, et. al., J. Anal. At. Spectrom., 2007, 22, 1051-1060.

Ashley, et. al., J. Environ. Monit., 2003, 5, 707-716.

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Boiano, et.al., J. Environ. Monit, 200, 2, 329-333.

California Environmental Protection Agency - Air Resources Board, SOP MLD39.



**To: Theresa Hosick, EPA/NEIC**

**Subject: Analytical Report on Analysis of Air Filter Samples for Hexavalent Chromium**

**Case No: EPA VP0591**

**From: Ruth E. Wolf, USGS**

**Date: June 24, 2008**

**Background:** Glass fiber air filters testing high in total Cr values were selected to be analyzed for Cr(VI) via HPLC ICP-MS using a method recently developed at USGS (Wolf et.al.). The samples need to be extracted or digested to release any Cr(VI) present with consideration to stabilizing any Cr(VI) liberated and preventing oxidation of Cr(III) present to Cr(VI).

**Sampling:**

One-inch sub-samples will be taken from each air filter (cut parallel to void areas left by filter holder) and accurately weighed to 0.1 mg. Each filter will be analyzed for Cr(VI) using a pH-buffered de-ionized water extraction procedure.

**Method Development:** The method developed at USGS for Cr(VI) has been used to determine Cr(VI) in natural waters, de-ionized water leachates of soil samples, and simulated gastric and lung fluid extracts of geological materials (Wolf, et. al., 2007). In summary, the method uses reversed-phase ion-pairing chromatography on a 3cm C8 column to separate the following species:  $\text{Cr}^{+3}$ ,  $\text{Cr}^{+6}$ ,  $\text{As}^{+3}$ ,  $\text{As}^{+5}$ ,  $\text{Se}^{+4}$ , and  $\text{Se}^{+6}$ . The HPLC mobile phase employed is 2 mM tetrabutylammonium hydroxide (TBAOH) with 0.5mM  $\text{K}_2\text{EDTA}$ , adjusted to pH 7.4 – 7.6. 5% methanol is added to the mobile phase by the HPLC pump. The EDTA present in the mobile phase is for the purposes of converting the Cr(III), which is present in aqueous solutions in a cationic form to an anionic Cr(III)-EDTA complex. All samples are diluted a minimum of 1:1 in the mobile phase and allowed to sit at room temperature to allow the Cr(III)-EDTA complex to form prior to analysis. Air filter samples had not been previously analyzed using this method, so some method development/validation work was undertaken to evaluate the efficacy of the method for use with glass and quartz air filter samples.

**Testing of soluble Cr(VI) Extraction Methods:** De-ionized water has been reported in the literature as an extractant for soluble Cr(VI) (Ashley, et.al.; OSHA Method ID-215, ver 2, Boiana, et. al.; and California EPA SOP MLD039); however, it has been noted that this method is problematic towards stability of Cr(VI). One possible issue is that the pH of DI-water is typically in the 6.0-6.5 range and Cr(VI) is easily reduced under even slightly acidic conditions. Studies at USGS have shown that using pH-adjusted DI-water as an extractant has a positive effect on Cr(VI) stability. Possible extraction solutions for soluble Cr(VI) will use DI-water adjusted to  $\text{pH} \geq 8$  using either a  $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$  buffer or  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$  buffer. Another possible extraction solution reported by Ashley, et.al., is a dilute ammonium sulfate-ammonium hydroxide buffer solution. All three buffer systems were tested prior to use with the analytical method reported by Wolf, et.al., to evaluate any potential interferences with the chromatographic separation or the detection method.

The following stock buffer solutions were prepared:

Buffer solution	Concentrations	Measured pH
Phosphate – pH 8	1 M $\text{K}_2\text{HPO}_4$ – 0.06M $\text{KH}_2\text{PO}_4$	8.4
Carbonate – pH 9	0.1 M $\text{Na}_2\text{CO}_3$ – 0.9 M $\text{NaHCO}_3$	9.2
Sulfate – pH 10	1M $(\text{NH}_4)_2\text{SO}_4$ – 1 M $\text{NH}_4\text{OH}$	10.3

In order to test their effect on the chromatographic separation, the buffers were diluted and mixed 1:1 with a 10 ppb multi-species stock solution containing  $\text{Cr}^{+3}$ ,  $\text{Cr}^{+6}$ ,  $\text{As}^{+3}$ ,  $\text{As}^{+5}$ ,  $\text{Se}^{+4}$ , and  $\text{Se}^{+6}$ . The following dilutions were run of each buffer solution:

Buffer ID	Diluted Total Concentration	pH	Results
20 mM $\text{CO}_3$	2 mM $\text{Na}_2\text{CO}_3$ – 20 mM $\text{NaHCO}_3$	9.1	Cr(III) – 1 min, Cr(VI) – 1.44 min
10 mM $\text{CO}_3$	1 mM $\text{Na}_2\text{CO}_3$ – 10 mM $\text{NaHCO}_3$	9.0	Cr(III) – 1 min, Cr(VI) – 1.44 min
20mM $\text{PO}_4$	20 mM $\text{K}_2\text{HPO}_4$ – 1 mM $\text{KH}_2\text{PO}_4$	8.2	Cr(III) – 1.1 min, Cr (unknown) 1.29, Cr(VI) – 1.49 min
10mM $\text{PO}_4$	10 mM $\text{K}_2\text{HPO}_4$ – 0.5 mM $\text{KH}_2\text{PO}_4$	8.1	Cr(III) – 1.13 min, Cr (unknown) 1.42, Cr(VI) – 1.56 min
50 mM $\text{SO}_4$	50 mM $(\text{NH}_4)_2\text{SO}_4$ – 50 mM $\text{NH}_4\text{OH}$	9.6	Cr(III) – lost?, Cr (unknown) 1.96, Cr(VI?) – 2.18 min
20 mM $\text{SO}_4$	20 mM $(\text{NH}_4)_2\text{SO}_4$ – 20 mM $\text{NH}_4\text{OH}$	9.5	Cr(III) – 0.92 min, Cr (unknown) 1.63, Cr(VI?) – 1.78 min

The use of the carbonate buffer resulted in no changes to the resulting chromatographic separation or detection with 2 clear peaks for chromium, Cr(III) at retention time of 1 minute and Cr(VI) at 1.44 minutes. The phosphate buffer system caused the chromatographic separation to change dramatically resulting in extra Cr peaks for some unidentified Cr species, possibly one of the other forms of Cr(VI). The use of the sulfate buffer caused a breakdown of the separation with several unidentified peaks and a high background where the normal Cr(III) and Cr(VI) peaks were expected. Based on this experiment, it was concluded that only the carbonate buffer system was a viable option for use with this separation and detection method. For all the extractions on prepared quartz filters, a 10 mM solution of the carbonate buffer was used (100x dilution of the prepared stock buffer solution).

**Testing of insoluble Cr(VI) extraction solutions :** After the initial pH-adjusted DI-water extraction for soluble Cr(VI), the filter sub-samples were to then be subjected to further extraction using a 3%  $\text{Na}_2\text{CO}_3$  – 2% NaOH solution heated to 95°C on a hot plate, hot block or hot water bath for 60 minutes (as reported by Ashley, et.al.), to extract any insoluble Cr(VI) left on the filter. This high pH sodium carbonate – sodium hydroxide extraction solution was also tested for its effects on the separation and detection method, and it was found that the chromatography was negatively affected by the extraction solution at even a 50X dilution. The results for a 10 ppb mixed species standard diluted 1:1 with a 1:50 fold dilution of the 3%  $\text{Na}_2\text{CO}_3$  – 2% NaOH extraction solution resulted in an extra peak showing up in the chromatogram for Cr(VI) – possibly one of the other Cr(VI) species known to exist or possibly from breakdown products of the Cr(III)-EDTA complex used to convert Cr(III) to an anionic form. As a result of this test, the solutions from the sample extraction in this high pH sodium carbonate – sodium hydroxide extraction fluid were not analyzed. The impact of this decision on



the analysis of the filter samples is that insoluble Cr(VI) compounds, if present, might not be extracted with the pH-adjusted DI water leach.

Buffer ID	Diluted Total Concentration	pH	Results
50X - 3% Na <sub>2</sub> CO <sub>3</sub> – 2% NaOH	0.06% Na <sub>2</sub> CO <sub>3</sub> – 0.04% NaOH	13	Cr(III) – 0.9 min, Cr (Unknown) – 1.23 min, Cr(VI) – 1.55 min, high blank background for Cr

**Preparation of Test Filters:** In order to test the suitability of the proposed extraction method, test samples were prepared as discussed in OSHA Method ID-215 by spiking blank quartz 45mm filters (Whatman #1851-047 Grade QMA, Lot #H11368033B) with solutions containing soluble and insoluble Cr(VI) and analyzing them as samples to evaluate extraction efficiency.

Prior to spiking, the filters were first prepared by treating them with 1N NaOH to enhance stability of Cr(VI). The filters were placed on a magnetic filter holder and using a vacuum filter dome, approximately 2mL of 1N NaOH was placed on the filter. The vacuum was turned on and the 1N NaOH solution pulled through the filter. The rinsed filters were removed from the filter holder with plastic forceps and placed on laboratory wipes, covered and allowed to dry overnight.

A purchased 1000 mg/L stock solution of Cr(VI) from K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (Spex Certiprep, NJ) was diluted to 10 mg/L with de-ionized water for use as a soluble Cr(VI) spiking solution.

A 100 mg/L solution of insoluble Cr(VI) was prepared from PbCrO<sub>4</sub> (Sigma, ACS Reagent grade, Lot 05315LC). The solution was prepared by dissolving 0.0624 g PbCrO<sub>4</sub> in hot 3% (w/v) Na<sub>2</sub>CO<sub>3</sub>-2% (w/v) NaOH and diluting to 100 mL with de-ionized water in a 100 mL volumetric flask.

Spiked filters were prepared by spiking a blank NaOH-prepared filter (NaOH-qtz) with a calculated amount of Cr(VI) from either the 10 mg/L K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution or the 10 mg/L PbCrO<sub>4</sub> and allowing the solution to air dry onto the filter prior to extraction. The filters were first put into the 50 mL centrifuge vial used for extraction (see below) and the solutions were spiked onto the filter. The filters were then allowed to dry in the refrigerator with the caps loose over the weekend.

Additionally, filter samples spiked with a micronized portion of NIST 2701 Hexavalent Chromium in Contaminated Soil (NJ Soil Cr(VI) SRM, in preparation by USGS for NIST), were also prepared by dusting a paintbrush dipped into the micronized soil over the surface of the filter while the vacuum was turned on. Approximately 60 mg of the micronized soil was loaded onto each filter.

**Sample Extraction Testing:** Each filter was carefully placed (by folding in half) into a 50 mL screw-cap polypropylene centrifuge vial and 50 mL of the 10mM sodium carbonate buffer solution was added (1 mM Na<sub>2</sub>CO<sub>3</sub> – 10 mM NaHCO<sub>3</sub>). The NaOH-qtz filter blanks and spikes were extracted at room temperature by sonication in a water bath for 3 hours. At the end of the sonication period the temperature in the water bath was approximately 60 ° C. The sample tubes were then removed to a rack and allowed to cool to room temperature prior to filtration.

Prior to analysis, a 10 mL aliquot of each supernatant (in some cases the tubes were centrifuged at 3000 rpm for 5 minutes beforehand) from the extraction tubes was drawn into a



10 mL disposable syringe (BD Dickenson). A 0.45  $\mu\text{m}$  syringe type filters (Pall, 25mm, Acrodisc, PDVF) was attached to the syringe and the extract was filtered into a new 15 mL polypropylene centrifuge tube.

**Analysis of test extracts:** Prior to analysis all filtered extract solutions were diluted a minimum of 1:1 with the HPLC mobile phase solution and allowed to sit at room temperature for approximately 30 minutes to allow the Cr(III)-EDTA complex to form. A second aliquot of each extract was also prepared and diluted 1:1 with the 10 ug/L mixed species calibration standard. The purpose of this second spiked aliquot was to act as an analytical spike. The recoveries of the species in the analytical spike was used to assess the impact of the sample matrix, if any, on the separation and could be used to account for any signal drift or enhancement due to the sample matrix over time. This was thought to be necessary since the instrument chromatographic software did not allow the use of a mass-spectral internal standard for multi-component analysis.

The extract solutions were analyzed according to the method reported by Wolf, et. al. If necessary, appropriate dilutions of the sample extracts were made in the HPLC mobile phase to reduce chromatographic interferences and reduce retention time shifts due to other sample constituents and buffer solutions. The ICP-MS was calibrated using aqueous stock solutions of As(III), As(V), Se(IV), Se(VI), Cr(VI) and Cr(III) calibration solutions (Spex Industries) and verified using a second source of stock standards (VHG Labs). Sample concentrations were calculated as ug Cr(VI)/ g filter.

**Results for Test Filter Samples:** The calculated percent recoveries for the analytical (post extraction) spikes of each test filter are given below. The first 4 rows are the results of analytical spikes on the blank mobile phase and sodium carbonate buffered DI-water leach solution. It should be noted that the Cr(VI) recoveries in these solutions range from 102 - 126%, indicating there may be some signal enhancement due to the carbonate buffer as compared to the 97% recovery observed in the mobile phase that did not contain the carbonate buffer. Analytical spike recoveries might possibly be used to correct for this signal enhancement, if deemed necessary.

<b>Analytical Spike Recovery for Test Samples</b>	<b>CrIII</b>	<b>CrVI</b>	<b>AsIII</b>	<b>AsV</b>	<b>SeIV</b>	<b>SeVI</b>
mobile phase blank spiked at 10 ppb	98.0%	96.6%	100.2%	98.8%	94.8%	101.8%
NaCO <sub>3</sub> leach blanks spiked at 10 ppb	96.4%	126.0%	99.2%	109.8%	109.4%	101.0%
Blank Filter 1	97.2%	101.6%	85.2%	116.0%	96.4%	94.0%
Blank Filter 2	104.0%	120.6%	84.2%	133.6%	105.8%	107.8%
Filter 3 - 1 ug sol Cr(VI) - 20 ppb in soln	104.2%	127.2%	83.6%	130.4%	108.2%	102.8%
Filter 4 - 1 ug sol Cr(VI) - 20 ppb in soln	106.4%	118.0%	80.6%	142.4%	106.6%	105.4%
Filter 5 - 1 ug insol Cr(VI) - 20 ppb in soln	103.4%	117.4%	81.2%	131.6%	107.6%	105.2%
Filter 6 - 1 ug insol Cr(VI) - 20 ppb in soln	102.4%	132.0%	80.6%	141.8%	110.6%	107.4%
Filter 7 - 2 ug insol+sol Cr(VI) - 40 ppb in soln	106.0%	117.8%	82.0%	137.8%	109.8%	106.6%
Filter 8 - 2 ug insol+sol Cr(VI) - 40 ppb in soln	100.8%	88.2%	85.2%	132.8%	106.2%	105.8%
Filter 9 - NIST 2701	105.2%	N/A	74.6%	152.0%	109.8%	108.4%
Filter 10 - NIST 2701	93.0%	N/A	72.0%	128.2%	99.0%	98.0%
<b>Average Analytical Spike Recovery</b>	<b>101.4%</b>	<b>114.5%</b>	<b>84.1%</b>	<b>129.6%</b>	<b>105.4%</b>	<b>103.7%</b>
<b>STD Deviation Analytical Spike Recovery</b>	<b>4.3%</b>	<b>14.3%</b>	<b>8.3%</b>	<b>14.9%</b>	<b>5.5%</b>	<b>4.4%</b>

The results for the test filters spiked with Cr(VI) solutions are given below:

Test Sample Description	CrVI	Adj for Anal. Spike Recovery
Filter 3 - 1 ug sol Cr(VI) - 20 ppb in soln	120.5%	94.7%
Filter 4 - 1 ug sol Cr(VI) - 20 ppb in soln	125.4%	106.3%
Filter 5 - 1 ug insol Cr(VI) - 20 ppb in soln	120.2%	102.4%
Filter 6 - 1 ug insol Cr(VI) - 20 ppb in soln	124.6%	94.4%
Filter 7 - 2 ug insol+sol Cr(VI) - 40 ppb in soln	127.0%	107.8%
Filter 8 - 2 ug insol+sol Cr(VI) - 40 ppb in soln	128.3%	145.5%
Filter 9 - NIST 2701	77.5%	N/A
Filter 10 - NIST 2701	77.8%	N/A

In general, it appears that all of the spike Cr(VI) was recovered from the filters, whether it came from the “soluble” form –  $K_2Cr_2O_7$  or the “insoluble” form –  $PbCrO_4$ . The slightly high recoveries are believed to be a result from signal enhancement due to the presence of sodium (~220 mg/L) which is enough to cause some signal enhancement in the ICP-MS. If the spiked filter recoveries were adjusted using the analytical spike recovery for each filter the recoveries are all within  $\pm 10\%$ , which is excellent, except for one sample of the 40 ppb spike level. It is expected that there might be some variation in the spike recovery of the two samples at 40 ppb, since the sample concentration is 4 times that of the spike concentration. The somewhat low recoveries for the NIST 2701 samples might be due to the large amount of sample that was loaded onto the filter. There was a significant amount of solid “soil” in the bottom of each test tube which had flaked off after the spiked filter was placed in the tube, rather than all of the sample remaining suspended on the filter. For the next round of testing a smaller amount of NIST 2701 will be loaded onto test filters.

**Preparation and Extraction of Air Filter Samples:** Samples were transferred from Theresa Hosick at EPA/NEIC to Ruth Wolf at USGS. The samples were maintained in a chain-of-custody location consisting of a file cabinet locked with a combination lock in the Research Chemistry ICP-MS Laboratory, G1302.

Sub-samples consisting of 1” portions of each filter were taken, weighed to the nearest 0.1mg and placed into clean polypropylene 50 mL centrifuge tubes. For quality control purposes, several spike NaOH-qtz filters were spiked with known amounts of Cr(VI) using stock  $K_2Cr_2O_7$  and  $PbCrO_4$  solutions as discussed previously. These QC samples were extracted along with the air filter samples. The samples were extracted in two sonicators (Branson 1500) for 3 hours at room temperature. The temperature of the water bath was taken at the end of the sonication period and had risen to 60°C. After sonication, the sample tubes were allowed to cool and were filtered as discussed previously using 25mm, 0.45  $\mu m$  pore size PVDF syringe filters and 10 mL disposable syringes into 15 mL centrifuge tubes. Lab numbers, sample numbers and weights are given below:



Lab ID	Sample ID	Sample wt (g)
QC1	45NaOHQtz + 50ug CrVI (K <sub>2</sub> CrO <sub>4</sub> )	
QC2	45NaOHQtz + 50ug CrVI (K <sub>2</sub> CrO <sub>4</sub> )	
QC3	45NaOHQtz + 50ug CrVI (K <sub>2</sub> CrO <sub>4</sub> )	
QC4	45NaOHQtz + 50ug CrVI (PbCrO <sub>4</sub> )	
QC5	45NaOHQtz + 50ug CrVI (PbCrO <sub>4</sub> )	
QC6	45NaOHQtz + 50ug CrVI (PbCrO <sub>4</sub> )	
QC7	45NaOHQtz + 100ug CrVI (K <sub>2</sub> CrO <sub>4</sub> +PbCrO <sub>4</sub> )	
QC8	45NaOHQtz + 100ug CrVI (K <sub>2</sub> CrO <sub>4</sub> +PbCrO <sub>4</sub> )	
S1	Blank Filter A (EPA 146680)	0.4698
S2	Blank Filter A duplicate (EPA 146680)	0.4573
S3	Blank Filter A spiked 1ug Cr(VI)	0.4558
S4	Blank Filter A spiked 1ug Cr(VI) Duplicate	0.4586
S5	Blank Filter B (EPA 146681 )	0.449
S6	Blank Filter B Duplicate (EPA 146681 )	0.4598
S7	Blank Filter B spiked 1ug Cr(VI)	0.4631
S8	Blank Filter B duplicate spiked 1ug Cr(VI)	0.4546
S9	EPA 146687	0.4935
S10	EPA 146358	0.4769
S11	EPA 146685	0.4786
S12	EPA 146363	0.5015
S13	EPA 146688	0.4735
S14	EPA 146688 Duplicate	0.4809
S15	EPA 146686	0.4803
S16	EPA 146686 Duplicate	0.485
S17	EPA 146684	0.466
S18	EPA 146683	0.4861
S19	EPA 146683 Duplicate	0.4952
S20	EPA 146682	0.4888
S21	NJ Soil - NIST 2701 (wt deposited)	0.0205
S22	NJ Soil Duplicate - NIST 2701 (wt deposited)	0.0261
S23	BCR 545	0.002908
S24	BCR 545 Duplicate	0.002956

**Analysis of Air Filter Extracts:** All sample extracts were diluted 1:1 with the HPLC mobile phase and allowed to sit at room temperature for 30 minutes prior to analysis to allow the Cr(III)-EDTA complexation reaction to occur. Note: it is expected that most, if any Cr(III) present in the extracts will be filtered out by the 0.45 µm filter as both soil and dust particles provide a host of charged particles that can result Cr(III) adsorption, including iron oxide particles which exist at pH>2. It has been previously observed that Cr(III) spikes in soils resulted in no Cr(III) recovery after the extracts had been filtered (see Wolf, et. al., 2007).

**Calibration:** The ICP-MS was calibrated using aqueous stock solutions of each species (Spex Certiprep) at 1, 2, 5, and 10 ppb. Analysis of low standards indicates that the detection limit of the method is 100 ng/L for all species and the Practical Quantitation Limit (PQL), determined by



the lowest standard level recovered within  $\pm 20\%$ , is 200 ng/L in the solution presented to the ICP-MS. The calibration curve was verified at 2 and 5 ppb at  $\pm 10\%$  recovery using a second source of commercially prepared stock solutions (VHG Labs) diluted to the appropriate concentration level.

**QC Sample Results:** The results for the prepared NaOH-qtz spiked QC filters are given below: In short all Cr(VI) was recovered and was slightly high due to uncorrected signal enhancement, believed due to the presence of the 200 ppm Na levels in the buffered sample extracts. If the recovery for a leach blank solution spiked with 10 ppb standard (120.8%) is used to ratio the QC spike recoveries, all recoveries are within  $\pm 15\%$ . Again, it appears that this sonication extraction procedure with the weak  $\text{Na}_2\text{CO}_3 - \text{NaHCO}_3$  buffer solution recovers Cr(VI) from both the “soluble” form –  $\text{K}_2\text{Cr}_2\text{O}_7$  and the “insoluble” form –  $\text{PbCrO}_4$ .

<b>QC Spiked NaOH-qtz filter results</b>	<b>Cr(VI) spike Recovery</b>	<b>Corrected Spike Recovery</b>
45NaOHQtz-1 + 50ug CrVI ( $\text{K}_2\text{Cr}_2\text{O}_7$ )	121.7%	100.7%
45NaOHQtz-2 + 50ug CrVI ( $\text{K}_2\text{Cr}_2\text{O}_7$ )	134.9%	111.7%
45NaOHQtz-2 + 50ug CrVI( $\text{K}_2\text{Cr}_2\text{O}_7$ )	129.7%	107.4%
<b>Average Recovery Cr(VI) from <math>\text{K}_2\text{Cr}_2\text{O}_7</math></b>	<b>128.8%</b>	<b>106.6%</b>
<b>RPD for replicate analysis</b>	<b>5.2%</b>	<b>5.2%</b>
45NaOHQtz-1 + 50ug CrVI ( $\text{PbCrO}_4$ )	129.1%	106.9%
45NaOHQtz-2 + 50ug CrVI ( $\text{PbCrO}_4$ )	125.0%	103.5%
45NaOHQtz-3 + 50ug CrVI ( $\text{PbCrO}_4$ )	137.5%	113.8%
<b>Average Recovery Cr(VI) from <math>\text{PbCrO}_4</math></b>	<b>130.5%</b>	<b>108.1%</b>
<b>RPD for replicate analysis</b>	<b>4.9%</b>	<b>4.9%</b>
45NaOHQtz-1 + 100ug CrVI ( $\text{K}_2\text{Cr}_2\text{O}_7 + \text{PbCrO}_4$ )	132.6%	109.8%
45NaOHQtz-1 + 100ug CrVI ( $\text{K}_2\text{Cr}_2\text{O}_7 + \text{PbCrO}_4$ )	129.2%	107.0%
<b>Average Recovery Cr(VI) from <math>\text{K}_2\text{Cr}_2\text{O}_7 + \text{PbCrO}_4</math></b>	<b>130.9%</b>	<b>108.4%</b>
<b>RPD for replicate analysis</b>	<b>1.8%</b>	<b>1.8%</b>
<b>Leach Blank with 10 ppb spike</b>	120.8%	

**Sample Results:** The results for the air filter samples for Cr(VI) are given in the tables below. The first table gives the Cr(VI) in  $\mu\text{g/g}$  filter based on the actual weight of the 1” filter sub-sample. Of noted significance are the recoveries for the 2 “real” QC sample materials. NIST 2701 which is soil highly contaminated with Cr(VI) was recovered at 107%. Also, tested was IRMM Certified Reference Material for Welding Dust Loaded on a PVC filter – BCR-545. This CRM was recovered as well with slightly high average recovery of 128%. If both of these reference materials are corrected for the analytical spike recovery, their recoveries are 88% for NIST 2701 and 105% for BCR-545, indicating that the extraction method is indeed recovering Cr(VI) present on these reference materials.

The second table gives the Cr(VI) results based on  $\mu\text{g}/\text{m}^3$  of the air flow going through the entire filter and compared to the total Cr results obtained independently by another laboratory. In summary, the Cr(VI) present in the filters is generally between 0.3 – 1.5% of the total Cr on the filter. It should be noted, however, that these were standard glass air filters and they had not been pre-treated as recommended for Cr(VI) analysis, nor were they analyzed within the recommended times in OSHA Method T-ID215, which appears to be 14 days for NaOH-qtz filters and 8 days if PVC filters are used. Thus, the concentrations of Cr(VI) listed are to be considered minimum values, present at the time of analysis after several months of storage time at room temperature and with exposure to air.

Sample ID	CrIII ug/g filter	CrVI ug/g filter	True Value ug/g	% Recovery Reference Sample
Blank Filter A (EPA 146680)	0	0.2152		
Blank Filter A duplicate (EPA 146680)	0	0.2264		
Blank Filter A spiked 1ug Cr(VI)	0	2.8176	2.011	128.1%
Blank Filter A spiked 1ug Cr(VI) Duplicate	0	2.8858	2.194	120.5%
Blank Filter B (EPA 146681 )	0	0.2333		
Blank Filter B Duplicate (EPA 146681 )	0	0.2938		
Blank Filter B spiked 1ug Cr(VI)	0	3.0174	2.159	128.5%
Blank Filter B duplicate spiked 1ug Cr(VI)	0	3.0174	2.2	126.1%
EPA 146687	0	0.1872		
EPA 146358	0.015699172	0.1008		
EPA 146685	0	0.2124		
EPA 146363	0.029858166	0.4107		
EPA 146688	0	0.5499		
EPA 146688 Duplicate	0	0.6197		
EPA 146686	0	0.1381		
EPA 146686 Duplicate	0	0.1209		
EPA 146684	0	0.1160		
EPA 146683	0	0.1324		
EPA 146683 Duplicate	0	0.1332		
EPA 146682	0	0.1720		
NJ Soil 2x (NIST 2701)	0	566.66	551.2	102.8%
NJ Soil Duplicate 2x (NIST 2701)	0	567.40	551.2	102.9%
NJ Soil 100x (NIST 2701)	0	599.97	551.2	108.8%
NJ Soil 100x Dup (NIST 2701)	0	698.23	551.2	126.7%
BCR545 B5-40 100x	0	56172.66	40200	139.7%
BCR545 B5-33 100x	0	48036.10	40200	119.5%
NJ Soil 50x (NIST 2701)	0	518.93	551.2	94.1%
NJ Soil 50x Dup (NIST 2701)	0	622.23	551.2	112.9%
BCR545 B5-40 50x	0	50292.70	40200	125.1%
BCR545 B5-33 50x	142.3960553	48184.79	40200	119.9%
NJ Soil 10x (NIST 2701)	0	566.21	551.2	102.7%
NJ Soil 10x Dup (NIST 2701)	0	591.88	551.2	107.4%
BCR545 B5-40 10x	0	51068.43	40200	127.0%
BCR545 B5-33 10x	0	53874.03	40200	134.0%

Ruth: Sample data are NOT blank subtracted..not sure if blanks were from same batch/lot as samples.

Sample Analytical Spike Average Recovery	107.3%	122.2%
Sample Analytical Spike Std Dev	7.4%	9.8%
Data are NOT corrected for spike recovery!		

Sample ID	CrIII ug/g filter	CrVI ug/g filter
Blank Average (EPA 146680, 146681)	0	0.242143272
std dev	0	0.035230274

EPA 146688 Average	0.584830666
EPA 146688 Std Dev	0.049371709
EPA 146686 Average	0.12950465
EPA 146686 Std Dev	0.01220044
EPA 146683 Average	0.132809525
EPA 146683 Std Dev	0.000564151

	Measured	Cert Value	% Rec
NJ Soil (NIST 2701) Average	588.6	551.2	107%
NJ Soil (NIST 2701) Std Dev	52.8	34.5	
BCR545 Average	51271.5	40200	128%
BCR545 Std Dev	3218.4	600	

Spike Recovery Adjusted Results			
	Measured	Cert Value	% Rec
NJ Soil (NIST 2701) Average	482.5	551.2	88%
NJ Soil (NIST 2701) Std Dev	43.3	34.5	
BCR545 Average	42025.8	40200	105%
BCR545 Std Dev	2638.0	600	

Note: Calibration standards were prepared in straight mobile phase (2mM TBAOH + 0.5mM K2EDTA) samples contained small amounts of NaCO3 buffer solution (1mM Na2CO3 + 9mM NaHCO3), calibration standards spiked with this buffer solution showed ~120% recovery - there might be some signal enhancement effect seen due to the presence of this buffer (most probably Na+). Internal standards were NOT used as chromatographic software can't handle this. Analytical spike data could be used to correct for this effect, if desired. If this correction is not done, the sample results could be ~20% high.



EPA COC Number	Filter #	Sample DATE	Total Flow m3	TSP ug/m3	initial wt (g)	final wt (g)	sample wt (g)	Total Cr ug/m3	Cr(VI) ug/m3
EPA 146687	G6017595	7/23/2007	2065	115	4.5937	4.8316	0.2379	0.064	0.00041
EPA 146358	G6017567	6/11/2007	2120		4.611	4.7628	0.1518	0.081	0.00021
EPA 146685	G6011536	12/19/2006	2228	93	4.5627	4.7702	0.2075	0.085	0.00042
EPA 146363	G6011508	11/7/2006	2160	167	4.566	4.9271	0.3611	0.13	0.00087
EPA 146688	G6017651	10/15/2007	2033	123	4.551	4.8014	0.2504	0.092	0.00117
EPA 146688 Duplicate	G6017651	10/15/2007	2033	123	4.551	4.8014	0.2504	0.092	0.00134
EPA 146686	G6017511	3/19/2007	2104	70	4.6171	4.7644	0.1473	0.06	0.00029
EPA 146686 Duplicate	G6017511	3/19/2007	2104	70	4.6171	4.7644	0.1473	0.06	0.00025
EPA 146684	G6010895	9/26/2006	2119	115	4.5426	4.7857	0.2431	0.07	0.00023
EPA 146683	G6011327	4/11/2006	2099	149	4.5239	4.8367	0.3138	0.062	0.00028
EPA 146683 Duplicate	G6011327	4/11/2006	2099	149	4.5239	4.8367	0.3138	0.062	0.00029
EPA 146682	G6011319	2/22/2006	2277	139	4.5597	4.8762	0.3165	0.096	0.00034

Filter Size: 8" x 10"

Estimated Total Deposit volume = 7" x 9.125"

17.78cm x 23.18cm

412.14 cm2

Ratio of sample flow/total Flow

0.1096

Estimated Deposit Volume on 1" strip: 1" x 7"

2.54cm x 17.78 cm

45.16 cm2

EPA COC Number	Filter #	Sample DATE	Cr(VI) ug/g filter	weight of 1" strip	ug Cr(VI) in sample	Adj Flow sample m3	Cr(VI) ug/m3	% Cr(VI)
EPA 146687	G6017595	7/23/2007	0.1872	0.4935	0.0924	226.3	0.000408	0.64%
EPA 146358	G6017567	6/11/2007	0.1008	0.4769	0.0481	232.3	0.000207	0.26%
EPA 146685	G6011536	12/19/2006	0.2124	0.4786	0.1017	244.1	0.000416	0.49%
EPA 146363	G6011508	11/7/2006	0.4107	0.5015	0.2060	236.7	0.000870	0.67%
EPA 146688	G6017651	10/15/2007	0.5499	0.4735	0.2604	222.8	0.001169	1.27%
EPA 146688 Duplicate	G6017651	10/15/2007	0.6197	0.4809	0.2980	222.8	0.001338	1.45%
EPA 146686	G6017511	3/19/2007	0.1381	0.4803	0.0663	230.5	0.000288	0.48%
EPA 146686 Duplicate	G6017511	3/19/2007	0.1209	0.4850	0.0586	230.5	0.000254	0.42%
EPA 146684	G6010895	9/26/2006	0.1160	0.4660	0.0541	232.2	0.000233	0.33%
EPA 146683	G6011327	4/11/2006	0.1324	0.4861	0.0644	230.0	0.000280	0.45%
EPA 146683 Duplicate	G6011327	4/11/2006	0.1332	0.4952	0.0660	230.0	0.000287	0.46%
EPA 146682	G6011319	2/22/2006	0.1720	0.4888	0.0841	249.5	0.000337	0.35%

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California Environmental Protection Agency - Air Resources Board, SOP MLD39.